

Performance of Lightweight Nickel Electrodes

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NICKEL ELECTRODES (NASA) 8 p CSCL 07D

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PERFORMANCE OF LIGHTWEIGHT NICKEL ELECTRODES

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SUMMARY

The NASA Lewis Research Center is currently developing nickel electrodes for nickel-hydrogen (Ni-H_2) batteries. These electrodes are lighter in weight and have higher energy densities than the heavier state-of-the-art (SOA) sintered nickel electrodes.

In the present approach, lightweight materials or plaques are used as conductive supports for the nickel hydroxide active material. These plaques (fiber and felt, nickel plated plastic and graphite) are commercial products that are fabricated into nickel electrodes by electrochemically impregnating them with active material. Evaluation is performed in half cells structured in the bipolar configuration. Initial performance tests include capacity measurements at five discharge levels; C/2, 1.0C, 1.37C, 2.0C, and 2.74C. The electrodes that pass the initial tests are life cycle tested in a low Earth orbit regime at 80 percent depth of discharge.

Different formulations of nickel fiber materials obtained from several manufacturers are currently being tested as possible candidates for nickel electrodes. One particular lightweight fiber mat electrode has accumulated over 3000 cycles to date, with stable capacity and voltage. Life and performance data of this electrode were investigated and presented. Good dimensional stability and active material adherence has been demonstrated in electrodes made from this lightweight plaque.

INTRODUCTION

The Nickel Hydrogen (Ni-H_2) technology group at NASA Lewis has been developing Ni-H_2 cells primarily for low-Earth-orbit (LEO) applications. The overall objective of the project is to improve the components, design, and operating characteristics of Ni-H_2 cells and batteries. The nickel electrode, in addition to being identified as the most critical component, has also been identified as the heaviest component of the Ni-H_2 battery system. NASA Lewis is developing nickel electrodes which will be lighter in weight and have greater specific energy than the state-of-the art (SOA) sintered electrode.

The experimental plaques that can be used to prepare electrodes are available commercially. These include a nickel fiber mat, Fibrex, from National Standard Co; a nickel coated graphite from American Cyanamid; a nickel felt mat from Sorapec; a nickel fiber mat from Nippon Seisen; and a plastic substrate from Amerace Corp. which was plated and developed at NASA Lewis (ref. 1). These materials are lightweight and have larger pore sizes than the SOA sintered plaque. Figure 1 shows the relative weights of the experimental nickel electrodes compared with the SOA sintered electrode. A reduction of about 58 percent in nickel electrode weight is possible by replacing the heavy sintered plaque with the lightweight plaques.

Initial cycle life experiments using the Fibrex mats are presently being performed and the results are very encouraging.

EXPERIMENTAL PLAQUES

The Fibrex nickel fibers are formed by reducing and sintering fibers extruded from a mixture of nickel oxide and binding agents (2). A special type of Fibrex mat that is layered with carbonyl nickel powder is currently being tested at NASA Lewis. This special type of material contains a 50:50 ratio of nickel fiber to nickel powder with 86 percent porosity, 30 mil thickness, and a density of 95 mg/cm².

Electrodes made from porous lightweight mats have a common feature of exhibiting a low initial utilization which gradually increases with cycling. This observation was detected in the earlier work on the nickel plated plastic at NASA Lewis (ref. 3) and the nickel composite electrode at Naval Surface Weapons Center (ref. 4). W. Lee (ref. 5) reported that the addition of cobalt hydroxide [Co(OH)₂] to the impregnated electrode will help to achieve full utilization of the Ni(OH)₂ active material earlier during cycling than in the untreated electrode. In an attempt to eliminate this added step, a special Fibrex material containing 50 percent nickel fiber, 35 percent nickel and 15 percent cobalt powder was prepared by National Standard. This special material has similar porosity, thickness and density as the original Co powder-free substrate.

ELECTROCHEMICAL IMPREGNATION

The substrates are electrochemically impregnated in an aqueous bath containing 1.5M Ni(NO₃)₂, 0.175M Co(NO₃)₂, and 0.075M NaNO₂ made acidic by the addition of 50 percent nitric acid (ref. 6). The bath is maintained at a constant temperature of 95 to 100 °C and a pH of 3 to 4. Prior to formation, a thin layer of Co(OH)₂ is deposited on the surface of the active material of the original electrode without Co powder added to the substrate. This procedure is done by dipping the impregnated substrate in the 1.8M Co(OH)₂ solution for 20 min, followed by treating with potassium hydroxide after the solution is drained off. This electrode will be called a Co-dipped electrode. The special electrode with Co powder added to the substrate was not treated with Co(OH)₂ solution. This electrode will be called a Co-substrate electrode. The aim of this experiment is to find out if the addition of the Co powder to the substrate itself will eliminate the need to soak the electrode in the Co solution.

The plaques are impregnated for various periods of time (2 to 5 hr) and current densities (50 to 93 mA/cm²) to determine the conditions needed to obtain the optimum loading level. A constant current density of 77.5 mA/cm² for 4 hr gave a loading level of 1.6 g/cm³ void of active material. The 1.6 g/cm³ void was selected as the loading level in order to compare the results with the existing data on the sintered nickel electrodes with similar loading levels. A 13 percent increase in thickness was measured when loading the Fibrex mats at this level. The electrode thickness increased as the loading level increased. The log-log plot of loading level versus percent thickness expansion is shown in figure 2. This straight line plot has a least square intercept of 0.94 and a slope of 1.1. The thickness expansion is

quantitatively related to the loading level by the following equation:
 $\log (\text{percent thickness expansion}) = 0.94 + 1.1 \log (\text{loading level})$

(1)

This initial expansion of the electrode during impregnation does not have any adverse effects on the performance of the electrode as long as there is no further significant expansion during cycling.

CYCLE LIFE TEST

The objectives of the cycle test are to obtain life data and to identify and evaluate any trends or degradation in electrode performance. The cycling tests include continuous cycling in a LEO regime (55 min charge, 35 minute discharge) at 80 percent depth-of-discharge. Approximately every 1000 cycles, capacity measurements are made by discharging to -0.2 V (versus a Hg/HgO reference electrode) at a 1.37C rate after charging for 80 min at a C rate. The percent utilization of the electrode is calculated by using the ratio of the measured capacity to the theoretical calculated capacity based on the weight of the active material deposited. The utilization of the Fibrex electrodes (Co-substrate and Co-dipped) are shown versus cycle life in figure 3. Initial utilization of the two types of Fibrex electrodes are comparable. However, it took about 150 cycles less for the Co-substrate electrode to reach its theoretical capacity. In addition, the utilization of the Co-substrate electrode is about 10 percent higher than that of the Co-dipped electrode.

The utilization of both types of electrode decreased gradually after over 3000 cycles. The Co-dipped electrode cycled for 3487 cycles before it reached its end of life. End of life or failure is defined as the point where the discharge voltage degrades to -0.2 V versus a Hg/HgO electrode. The capacity decrease of this electrode at the end of the cycle test was 23 percent. The thickness of the electrode measured after the cycle life test increased by about 13 percent from the initial electrode thickness (over and above the increased thickness after the impregnation process). The Co-substrate electrode continues to cycle with stable voltage with over 3500 cycles to date.

ELECTRODE PERFORMANCE AT DIFFERENT RATES

Figures 4 and 5 depict the performance of the two different types of Fibrex electrodes at the different discharge rates. The initial utilization is defined as the cycle where the electrodes reach their theoretical capacity (cycle 268 for Co-dipped electrode and cycle 111 for the Co-substrate electrode). The data shows the initial capacity values for all the discharge rates for both electrodes. As the electrodes cycle, the capacity decreased as the discharge rate increased. The cell capacities depended on the discharge rate and showed lower capacities at the higher rate. The cell capacity at the high rate of the Co-dipped electrode decreased at the faster rate than that of the Co-substrate electrode during cycling. After 3400 cycles, the utilizations of the Co-dipped and Co-substrate electrodes at the 2.74C rate decrease 33 and 17 percent respectively from the initial measurement. The Co-substrate electrode, after 3400 cycles, has 23 percent better utilization than the Co-dipped electrode at the high rate. At the lower rate though, the utilization is about the same. There is no sign of any deterioration in the low rate capacities of either electrode after being cycled. At the end of life (cycle 3487), the capacity of the Co-dipped electrode at the 2.74C rate

is 30 percent less than the initial value at the same rate while the capacity at the C/2 rate did not decrease at all as shown in figure 4. This signifies that the failure of the electrode is due to the loss of high rate discharge capacity rather than the loss in total electrode capacity.

PORE SIZE DISTRIBUTION

The pore size distribution of the Ni electrodes was measured using mercury intrusion porosimetry. Figure 6 shows the pore size distribution curves of the Co-dipped Fibrex electrode. The new and cycled electrodes have similar pore size peaks but cycling to failure increases the total pore volume which is probably due to the expansion of the electrode. The traditional increase in the volume of the small radii found in cycled SOA nickel electrodes, as shown in figure 7 (ref. 7), is not observed in the Fibrex electrode. This large increase in the micropore volume of the SOA nickel electrode results in the electrode having a greater affinity for the electrolyte. This effect can dry the separator and will lead to a high separator resistance. The pore size distribution of the cycled Fibrex electrode (fig. 6) shows a distinct multiple peak profile from 0.01 to 8 μm as opposed to the minimal peak profile of the SOA electrode across the same region. In addition to a two-fold increase in volume of the micropores as the Fibrex electrode is cycled, the volume of the larger pores (over 9 μm) is increased 3 to 5 times. This indicates that the Fibrex electrode will not compete with the separator for electrolyte because of the electrode's bimodal pore size distribution.

CONCLUSIONS

Improving the performance and cycle life as well as increasing the specific energy of the Ni-H₂ cells are the drivers of the technology development program at NASA Lewis. One means of achieving these goals is by developing lightweight nickel electrodes. Our studies show that as much as 58 percent reduction in electrode weight can be achieved.

Electrochemical impregnation of the Fibrex mats, from an aqueous bath of nickel nitrate-cobalt nitrate, yields loading levels comparable to SOA nickel electrodes.

The Fibrex Co-substrate electrode has a better overall performance than the Co-dipped electrode. The major performance change of the Fibrex electrodes during cycling is the decrease of the high rate discharge capability rather than the decrease in the total capacity.

Expansion of the Fibrex electrode after cycling is about 25 percent less than the SOA nickel electrodes. The expansion in the SOA electrodes results in poor electrolyte distribution in the Ni-H₂ cell which has been considered to be one of the major failure modes of the cell. The bimodal distribution of the cycled Fibrex electrode should reduce this problem.

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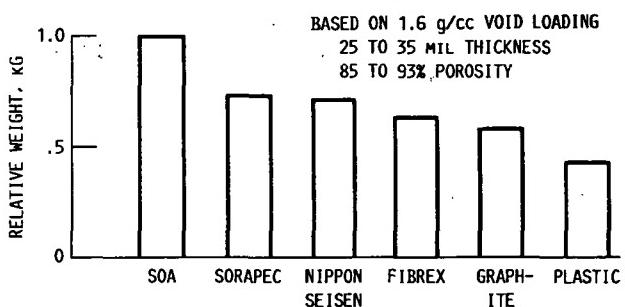


FIGURE 1. - RELATIVE WEIGHTS OF SOA AND LIGHTWEIGHT ELECTRODES.

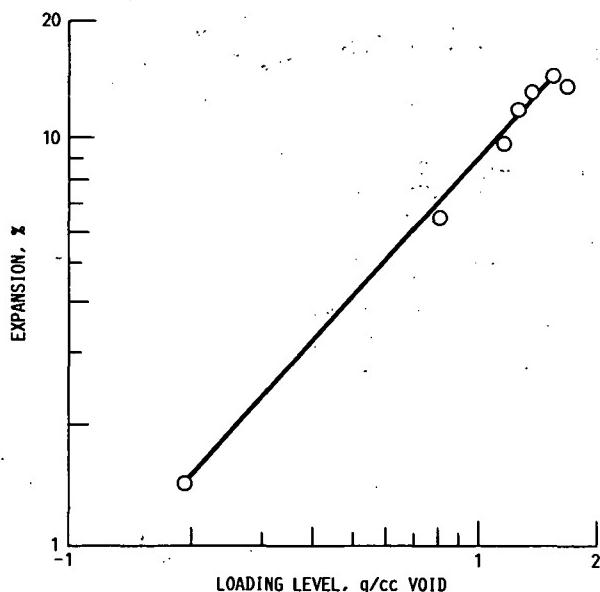


FIGURE 2. - LOG-LOG PLOT OF THE LOADING LEVEL VERSUS THICKNESS EXPANSION OF FIBREX NICKEL ELECTRODE.

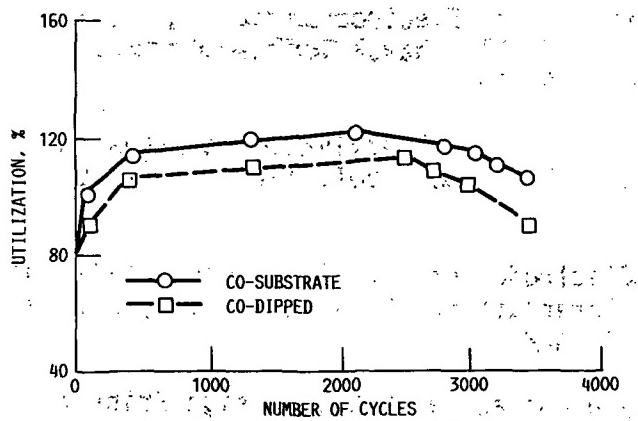


FIGURE 3. - CYCLE-LIFE DATA OF FIBREX NICKEL ELECTRODE.

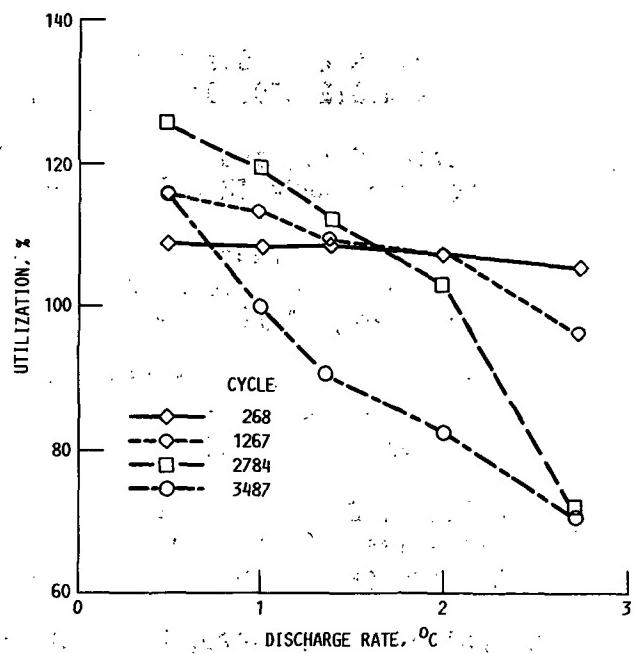


FIGURE 4. - UTILIZATIONS OF CO-DIPPED NICKEL ELECTRODE AT VARIOUS DISCHARGE RATES AND CYCLES.

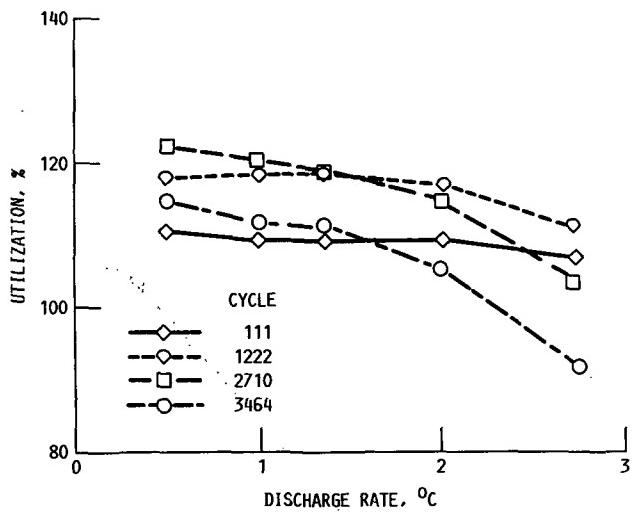


FIGURE 5. - UTILIZATIONS OF CO-SUBSTRATE NICKEL ELECTRODE AT VARIOUS DISCHARGE RATES AND CYCLES.

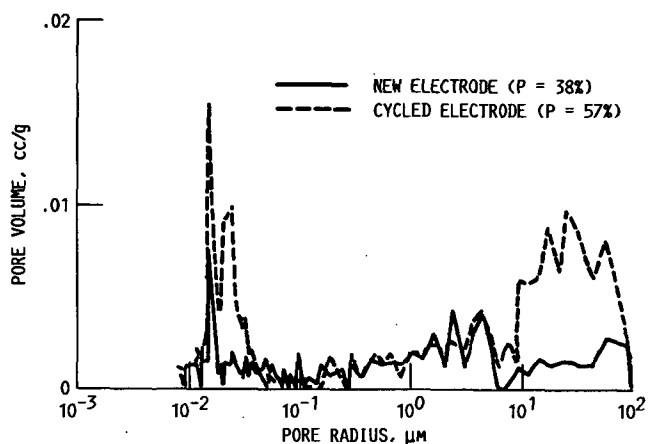


FIGURE 6. - PORE SIZE DISTRIBUTION CURVES OF NEW AND CYCLED CO-DIPPED FIBREX NICKEL ELECTRODE.

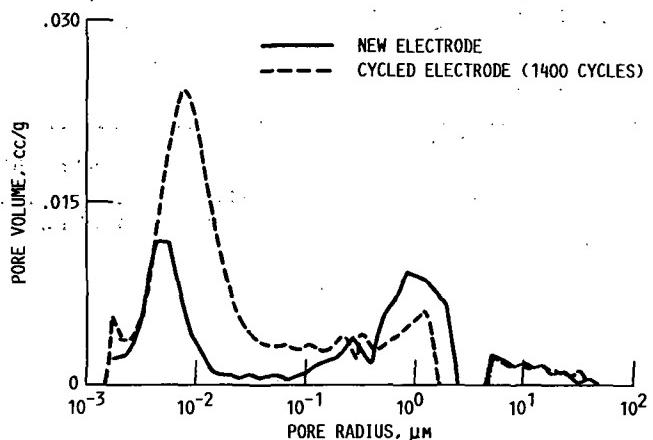


FIGURE 7. - PORE SIZE DISTRIBUTION CURVES OF NEW AND CYCLED SOA NICKEL ELECTRODE.



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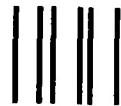
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